"Abnormal Changes in some Lines in the Spectrum of Lithium."

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Communicated by Professor G. D. Liveing, F.R.S. Received November 19,—Read December 11, 1902.

In the course of an investigation on the flame spectra of metals, the writer has examined the spectrum of lithium. Some facts have been discovered of sufficient importance for a separate paper.

The same spectrometer was used as in the investigation on the "Spectra of Potassium, &c."* Whilst the wave-lengths of some of the lines in the flame spectrum of lithium agree closely with those given by Kayser and Runge for the lines in the arc spectrum,† the wave-lengths of other lines differ considerably from these. The numbers and differences are given in the following table:—

Oxyhydrogen flame spectrum (Author).		Arc spectrum (Kayser and Runge).					
		Principal series.		Second subordinate series.		First subordinate series.	
Wave-length.	Intensity.	Wave-length.	Difference from flame.	Wave-length.	Difference from flame.	Wave-length.	Difference from flame.
6708	10	6708·2	—				
6103·84	9					6103·77	−0·07
4971·98	2			4972·11	+0·13		
4603·07	7					4602·37	−0·70
4273·34	1			4273·44	+0·10		
4132·93	5					4132·44	−0·49
3985·86	<1			3985·94	+0·08		
3915·59	3					3915·2	−0·39
3795·18	2					3794·9	−0·28
3719	1					3718·9	—
3232·82	4	3232·77	−0·05				
2741·43	1	2741·39	−0·04				

The flame lines are all sharp.

Kayser and Runge describe the lines 6708·2, 3232·77, 2741·39, and 6103·77 as "mostly reversed"; the lines in the second subordinate series as diffuse towards the red; the lines 4602·37 and 4132·44 as reversed; and the latter, with the remaining lines in the same, series as diffuse on both sides.

* 'Roy. Soc. Proc.,' vol. 70 (1902), p. 303.

† 'Berlin Akad. Abhandl.' (1890), vol. 4, p. 19.

The only important differences occur in the lines of the first subordinate series. Exner and Haschek have given the wave-lengths of three lines in the spark spectrum* as 2815·55, 3232·91, and 4603·10. The last is described as reversed. Eder and Valenta have given the wave-length of the blue line in the Bunsen flame spectrum as 4602·4,† and as 4602·46 in the spark spectrum when a condenser was used.‡ They described the latter measurement as that of the middle of a broad dark line, the less refrangible wing of which was stronger than the other, and diffuse towards the red. They also gave measurements of five other lines, and these agree closely with the arc lines given by Kayser and Runge. Professor Hartley recorded four lines in the oxyhydrogen flame spectrum of lithium chloride§ corresponding to the first, fourth, sixth and eleventh of the lines in the above table. The blue line was measured in the flame spectrum on four plates, and the results differed only in the second decimal place, the figures in which were 8, 7, 6 and 7. Professors Liveing and Dewar made some observations by eye on the appearance of the blue line in the arc spectrum which led them to believe there were two lines, a strong one with a weak line on the more refrangible side,|| and Kayser and Runge, after referring to this, say :—¶ " Wir haben nur bei zwei Aufnahmen neben der Hauptlinie eine zweite schwache umgekehrte Linie bei 4603·13 erhalten ; da aber hier eine Eisenlinie liegt, glauben wir, dass dies eben die Eisenlinie ist, welche sich durch den hellen Hintergrund der Lithiumlinie umgekehrt hat."

The wave-length of the line which Kayser and Runge attributed to iron agrees with that obtained by the author for the bright line in the flame spectrum, and by Exner and Haschek for the reversed line in a spark spectrum. It was decided in view of these differences to take a series of photographs of the arc spectrum of lithium, using the carbonate of lithium on carbon poles, and to study especially the appearances of the blue line. The results will now be briefly described.

A Gulcher arc lamp with vertical carbons was used. When the arc was started with a quantity of lithium carbonate on the carbons, a large proportion of the salt was freely volatilised and expelled in the form of a dense vapour. As the arc lamp was placed, the magnetic field produced by the feed mechanism caused the bulk of the vapour to be expelled in the direction of the collimator. Photographs of the spectrum taken at this early stage show the line as a very broad bright line extending from 4610·4 to 4593·5, with a narrow dark line extend-

* 'Sitzber. kais. Akad. Wien,' vol. 106, Abth. 2A (1897), p. 1133.

† 'Denkschr. kais. Akad. Wien,' vol. 60 (1893).

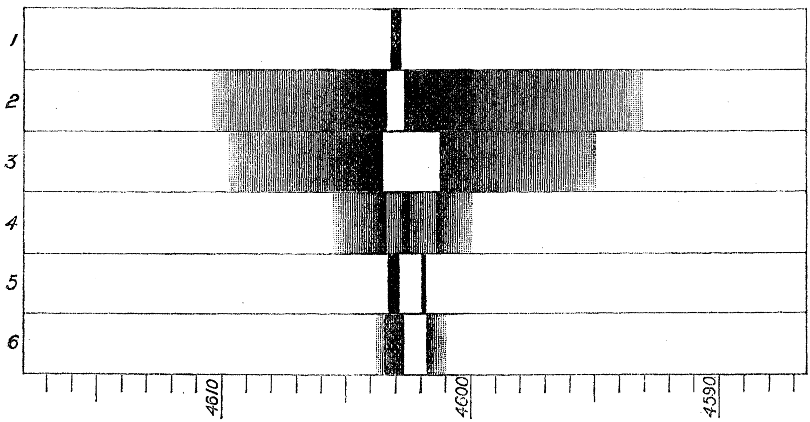
‡ 'Denkschr. kais. Akad. Wien,' vol. 67 (1898).

§ 'Phil. Trans.,' A, vol. 185 (1894), p. 177.

|| 'Phil. Trans.,' vol. 174 (1883), p. 215.

¶ *Ibid.*, p. 20.

ing (2 in figure) from 4603·46 to 4602·71, having its middle (measured) at 4603·06. The middle of the broad bright line is, according to the above, at wave-length 4601·95, and the middle of the dark line (reversed) is coincident with the bright line of the flame spectrum.



Diagrams of the blue lithium line as it appears in photographs. The fine vertical lines are merely shading lines; the broad wings of the actual lines in the spectra are continuous.

(1) Bright line of flame, arc and spark spectra.
(2) Reversed line from dense outer flame of arc.
(3) Reversed line from inner cone of strong arcs and from near negative pole of weak arcs.
(4) Broad line with two absorption bands, from arc spectrum.
(5 and 6) From spectrum of thin outer flame of arc with different exposures.

One pole of a weak bar magnet was placed near the arc so as to direct the expelled vapour in a direction perpendicular to the axis of the collimator. After the large excess of the lithium salt had been volatilised the image of the central portion of the arc was thrown on the slit, and the spectrum photographed, when the ends of the carbon poles, not widely separated, were red-hot. The lithium vapour in the central core was doubtless at a very high temperature, and there was only a thin layer of cooler vapour between it and the slit. Under these conditions the bright line is again broadly expanded, and so also is the dark line, for it now extends from 4603·55 to 4601·25 (mean = 4602·40) on one photograph (3 in figure), and from 4603·68 to 4601·22 (mean = 4602·45) on another. The bright wings are nearly of the same intensity and extent. The middles of these two dark lines are nearly the same as the wave-length 4602·37, given by Kayser and Runge, and by Eder and Valenta for the reversed lines.

Some photographs were also taken of the spectrum of the transparent flame which issued from the arc, the bar magnet being used as above. With a short exposure one narrow bright line was obtained of wave-length 4603·06; with a longer exposure this bright line was much stronger, and there was the appearance of a weak line on its more refrangible side, exactly as Professors Liveing and Dewar described. The wave-lengths of these two were 4603·18 and 4601·89 respectively on one photograph (5 in figure), and 4603·12 and 4601·65 on another. The last line was fairly sharp on the less refrangible side, whilst it faded gradually on the other side (6 in figure). With still longer exposures the weaker line could not be distinguished from the wing of the much expanded bright line. This wing when weak always resembles a line, and it was thought that a line might be nearly coincident with its less refrangible edge. Measurements showed that this edge varied in position on different photographs, but Professor Liveing suggested that the tip might be formed by a line, and if so, the tip should always have the same wave-length. The following table gives the wave-lengths of the two tips on different photographs:—

Spectrum.	Tip of weaker side.	Tip of stronger side.
206^3	4601·68	
213^4	·83	4603·11
213^6	·66	·11
214^1	·72	·03
222^6	·78	·10
222^7	·82	·11
224^6	·82	
226^5	·83	
226^7	·95	4603·21
232^6	·79	

This evidence is not conclusive; both tips appear to vary, but the weaker one varies more than the other. The arc, in these experiments, was formed with a Gulcher lamp with the carbons vertical, the positive being uppermost, and the image of the arc projected on to the slit of the collimator by a lens. It was observed that the less refrangible point, wave-length 4603·1, was, in many photographs, higher on the plate than the weaker point; it was given out by vapour quite near to the positive pole. It was observed also in some photographs that the line extending from it faded away lower down; the vapour near the negative pole did not emit this line but gave the broad bright line with the broad dark line down its middle. This broad bright line fades away as the positive pole is approached; the more refrangible wing ends in a point, but the less

refrangible wing is lost in the bright line of wave-length 4603·1. There appears then in the middle portion of the spectrum a broad dark line with wings of unequal extent, and the less refrangible wing is broader, and, near its more refrangible edge, much stronger than the other wing. The broad dark line extended on such photographs from (1) 4602·72 to 4601·81, (2) 4602·86 to 4602·05, (3) 4602·73 to 4601·62, and in two other cases, where there were less differences of intensity between the two wings, from 4603·26 to 4601·61 and from 4603·07 to 4601·59. There were indications on some photographs of a bright line near the middle of the broad dark line; the measurements of such a photograph gave :—

Less refrangible edge of broad dark line	4603·40
Apparent bright line	4602·57
More refrangible edge of broad dark line......	4601·31

The absorption bands of reversals in such a photograph as this are comparatively bright, for there is considerable action on the plate where the images of these bands fall (4 in figure). The effect is probably due tothe superposition of the spectrum of the outer flame upon that of the inner core when both are giving reversed lines.

Some observations were made at Professor Liveing's suggestion on the arc spectrum of lithium when the arc was formed between carbon electrodes inserted horizontally in a magnesia brick. The arc enclosed in this way is much steadier than in the open. The light which was examined passed out through a horizontal hole perpendicular to the carbons. The differences described above between the spectra of the vapours near the two poles were easily observed by eye observations.

Photographs of the spark spectra of lithium were taken in the hope of finding a second line which would account for the remarkable differences in the arc spectra, but no second line was found. A piece of metallic lithium was placed in a cup formed in the end of an aluminium rod, and sparks were passed between this and an aluminium wire held immediately over the lithium. No Leyden-jar was put into the secondary circuit at first, and it was found that photographs of the blue line were obtained with exposures of 15 minutes. The lines were sharp, and showed no signs of reversal. The wave-length of the blue line was found to be 4603·08. The vapour near the electrodes gave broader lines than the vapour a short distance away. The broadening was much greater at the negative electrode than the positive, and it extended further on the more refrangible side than on the other side. The bright line and the broad reversed line were, in fact, both present in the spectrum of the spark, near the negative electrode.

It was much more difficult to obtain photographs of the spark spectrum when a Leyden jar was introduced. Some were obtained from

moist lithium carbonate which had been fused into the aluminium cup. The blue line was very weak and nebulous, and it was difficult to obtain measurements of it. The following were obtained from four photographs :—4603·18, 4603·14, 4602·99 and 4603·97; the mean of these is 4603·15. Better photographs were obtained when a coil of wire was also introduced into the secondary circuit. The line more nearly resembled that obtained when no Leyden jar was used; the broad reversed line was more clearly defined at the electrode when negative than when positive.

An attempt was made to photograph the blue line in the Bunsen flame spectrum, but with an exposure of six hours no trace of it was obtained.

Other lines in the Spectrum of Lithium.

The orange line was examined in the arc and flame spectra by eye observations and by photography. The line in the flame spectrum was measured on four plates :—

Spectrum.	Wave-length.	
244^2	6103·84	centre of line.
244^2	6103·85	near tip of line.
244^4	6103·88	rather strong line.
245^2	6103·84	
245^3	6103·83	

The mean of these, omitting the rather strong line, is 6103·84. None of these lines showed any signs of reversal.

The wave-length of the bright line in the arc produced by the Gulcher lamp in the open was :—

Spectrum.	Wave-length.	
241^6	6103·81	nebulous in middle with sharp points. The nebulous part extended from 6102·46 to 6104·94.
242^4	6103·86	
242^5	6103·82	

The mean result is 6103·83.

The orange line is easily reversed in the arc. The reversed line was photographed and the wave-length measured on two plates, the results being 6103·82 and 6103·84. The reversal was narrow and the wings did not extend very far. The more refrangible wing was slightly broader than the other, and this difference was observed in the photographs and by eye observations. The part of the arc near the negative pole was examined very carefully; the line was most sharply reversed in that part, but there was no trace of a broad dark line. The orange line, with the exceptions noted, behaved normally.

Measurements were also made of two other lines in the arc spectrum. The wave-length of a weak and very diffuse line on one plate was 4132·82, and that of a very weak sharp line, 4273·32. The former line on another plate was stronger and broader; its middle was at 4132·35, whilst the other line, much broadened towards the red, had its strongest part at 4273·62.

The current used in working both the open and enclosed arcs was about 9 ampères. Kayser and Runge employed a current of 25—35 ampères from one machine and, to bring out the weak lines in some spectra, a current of 40—50 ampères from another machine. It seems probable that they worked with the intense arc which was only obtained by the author when the carbons were very near together, and that they observed only the spectrum of broadened lines which the author found was emitted by the intense arc and near the negative pole by weaker arcs. Their remarks on the appearances of the lines in the first and second subordinate series confirm this view. Eder and Valentà obtained a similar spectrum to Kayser and Runge's arc spectrum in the spark spectrum of metallic lithium when they used a condenser in the secondary circuit.

The author has pleasure in thanking Professor Liveing for the interest he has taken in this work and for some useful suggestions.

Conclusions.

The lines in the principal series of lithium appear to broaden and reverse normally.

The lines in the second subordinate series do not reverse even in the arc, but in strong arcs they broaden towards the less refrangible end of the spectrum and become diffuse on that side.

The first line in the first subordinate series, wave-length 6103·84, is almost normal; it broadens slightly more on the more refrangible side than on the other. The other lines in this series also broaden on both sides and become diffuse, but they broaden more rapidly on the more refrangible side than on the other. The centres of the broadened lines are more refrangible than the corresponding lines in the narrow state. The inner core of intense arcs, and the parts near the negative poles of weak arcs and sparks, give a broad reversed line with its centre about wave-length 4602·4; whilst the part near the positive pole in weak arcs, and the flame of the arc, give a sharp bright line, wave-length 4603·07, coincident with the lines in the spectra of the oxyhydrogen flame and uncondensed spark. The similar changes in the other lines diminish with their refrangibility. The wave-lengths hitherto recorded for these diffuse lithium lines would appear to be those of abnormal lines. The true lines are the sharp bright ones which occur, without complication, in the spectrum of lithium in the oxyhydrogen flame.

[ADDED NOV. 28, 1902.—Since this paper was communicated to the Royal Society, I have seen a paper on the spectrum of lithium, by Hagenbach, in the 'Annalen der Physik,' No. 12, 1902, which was published on November 13. The experimental part of his paper deals almost entirely with the blue line, and the fact that there are other abnormal lines in the spectrum of lithium is recorded above for the first time. Hagenbach's conclusion that there are two lines near wavelength 4603 is not, I think, established; and I still hold that the views expressed in this paper are more probable. He has not been able to find the second line as a bright line, so the difficulties in the way of accepting the view that there is a second dark line, without a corresponding bright line, remain. He has not referred to Professors Liveing and Dewar's work,* and his evidence for saying there are two lines is, in fact, similar to the evidence they gave.]

'An Error in the Estimation of the Specific Gravity of the Blood by Hammerschlag's Method, when employed in connection with Hydrometers." By A. G. LEVY, M.D. (London). Communicated by Sir VICTOR HORSLEY, F.R.S. Received November 25,—Read December 11, 1902.

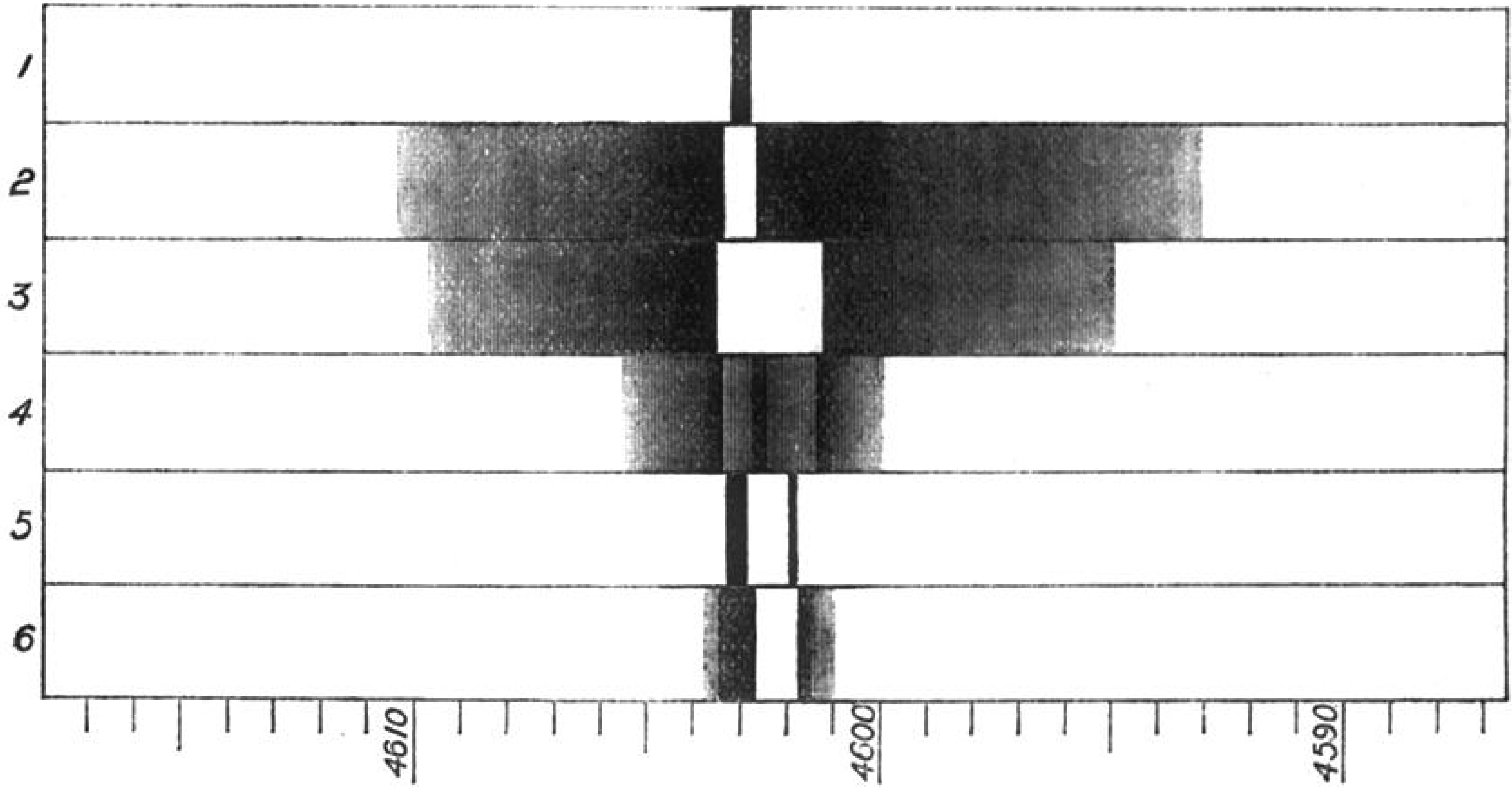
(From the Laboratory of Pathological Chemistry, University College, London.)

Hammerschlag's method of estimation of the specific gravity of the blood is an application to clinical purposes of a physical method frequently employed when only a small quantity of the substance under investigation is obtainable. The method may be briefly described as the adjustment of the specific gravity of a mixture of chloroform and benzol by small successive additions of either constituent until it corresponds to the specific gravity of the blood, the test of the attainment of this condition being that a small drop of the blood, when immersed in the mixture, shall remain suspended without any very obvious tendency to rise or sink. The specific gravity of the mixture is then estimated by means of a hydrometer, the scale of which is graduated to register densities lying between the maximum and minimum densities of blood, *i.e.*, from 1·020 to 1·080.

In order to attain a rapid adjustment of the relative proportions of the chloroform and benzol, it is the general practice to use a comparatively small quantity only of these fluids and a small hydrometer, and, as will be hereafter seen, the size of the instrument is an important factor in the magnitude of the error.

This error was commented upon in a paper read by Dr. Baumann

* 'Phil. Trans.,' vol. 174 (1883), p. 215.



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